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Effect of γ -ray irradiation on mechanical properties of PVA and acetalized PVA films. Ichiro Sakurada, Waichiro Tsuji and Fujiko Kimura. *Kobunshi Kagaku*, **18**, 396 (1961), in Japanese.—Effect of irradiation on tensile strength and elongation of PVA and acetalized PVA films has been studied. The filaments were irradiated at room temperature in vacuo and in air. Tensile strength of PVA films heat-treated at 140° C increases by about 15 % by irradiation and that of the films heat-treated at 200° C remains almost unchanged whereas elongation of these films decreases with increasing radiation doses. Tensile strength and elongation of acetalized PVA films decrease remarkably with increasing doses, and the decrement is larger where the films were irradiated in air than in vacuo.

Effects of cobalt-60 gamma radiation on poly(vinyl alcohol). 3. Effects of gamma radiation on water-swollen films and aqueous solutions. Ichiro Sakurada and Yoshito Ikada. *Bull. Inst. Chem. Res., Kyoto Univ.*, **39**, 99 (1961).

Effects of γ -ray irradiation on filament of isotactic polypropylene. Ichiro Sakurada and Fujiko Kimura. *Bull. Inst. Chem. Res., Kyoto Univ.*, **39**, 226 (1961).

Polymerization of ketene and diketene. Ryohei Oda, Sunao Munemiya and Masaya Okano. *Makromol. Chem.*, **43**, 149 (1961).—See, this Bulletin, **39**, 413 (1961).

Preparation of crystalline polyaldehydes. Junji Furukawa, Takeo Saegusa and Hiroyasu Fjii. *Makromol. Chem.*, **44**, 398 (1961).—See, this Bulletin, **39**, 325 (1961).

Polymerization of acetaldehyde. Junji Furukawa, Takeo Saegusa and Hiroyasu Fujii. *Bull. Japan Petrol. Inst.*, **3**, 33 (1961).—See, this Bulletin, **39**, 413 (1961).

Polymerization of alkylene oxides. Junji Furukawa, Takeo Saegusa and Teiji Tsuruta. *Bull. Japan Petrol. Inst.*, **3**, 39 (1961).—See, this Bulletin, **39**, 414 (1961).

Concept of covalent and polar nature in chemical bonds and its application to radical reaction. Junji Furukawa. *Bull. Inst. Chem. Res., Kyoto Univ.*, **39**, 1 (1961).

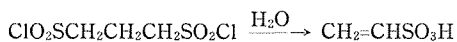
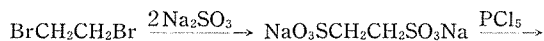
Kinetic interpretation of rheological behavior of high polymers. Junji Furukawa. *Bull. Inst. Chem. Res., Kyoto Univ.*, **39**, 20 (1961).

Organic Chemistry

New addition reactions. I. Reaction of epoxides with ketene. Ryohei Oda, Sunao Munemiya and Masaya Okano. *J. Org. Chem.*, **26**, 1341 (1961).—See, this Bulletin, **39**, 413 (1961).

Studies on vinyl sulfonic acid. 1. Synthesis of vinyl sulfonic acid and the monomer reactivity ratio and dyeability of its copolymer with acrylonitrile. Sango Kunitika and Takao Katagiri. *Kogyo Kagaku Zasshi*, **64**, 929 (1961), in Japanese.—

After being tried to prepare vinyl sulfonic acid (VS) by various methods, it was found that the following process was the best for the laboratory scale :



To find the monomer reactivity ratios (MRR), VS was copolymerized with acrylonitrile (AN). By the Fineman-Ross method, MRR were found as $r_1=1.5$ (AN) and $r_2=0.15$ (VS). From these data the Q and e values of VS were estimated as $Q=0.09$ and $e=+1.3$. The dyeability of AN-VS copolymers to the cationic dye was very good as the authors expected. The initial adsorption rate was very high on the copolymer containing 4.3 mole % of VS.

Studies on vinyl sulfonic acid. Sango Kunichika and Takao Katagiri. *Bull. Inst. Chem. Res., Kyoto Univ.*, **39**, 215 (1961).

Studies on lactone formation in vapor phase. I. Synthesis of γ -butyrolactone. Shinzaburo Oka. *Bull. Chem. Soc. Japan*, **34**, 12 (1961).—See, this Bulletin, **41**, 220 (1961).

Synthesis of γ -valerolactone. Shinzaburo Oka. *Bull. Inst. Chem. Res., Kyoto Univ.*, **39**, 322 (1961).

The influence of solvent and metal ion on the rate of reaction of alkali metal borohydrides with acetone. Herbert C. Brown and Katsuhiko Ichikawa. *J. Am. Chem. Soc.*, **83**, 4372 (1961).—In water, ethanol and isopropyl alcohol the rate of reaction of sodium borohydride with acetone exhibits second-order kinetics, first order in each of the two reactants. The rate constants at 0° are (10^{-4} l. mole⁻¹ sec.⁻¹) 93 in water, 97 in ethanol and 15.1 in isopropyl alcohol. The addition of lithium chloride in water has no effect upon the rate, whereas in isopropyl alcohol the rate constant increases by a factor of three, to 50.3. Moreover, the rate constant increases with increasing concentrations of lithium halide. These results indicate that in water the reaction involves the dissociated borohydride ion, whereas in isopropyl alcohol the reacting species must be the ion pair, M^+BH_4^- . In aprotic solvents, such as acetonitrile, pyridine, dimethylformamide and diglyme, no detectable reaction of sodium borohydride with acetone was observed at 0°. Consequently, the ability of the solvent to ionize must be involved in the mechanism of the reaction between the borohydride and the ketone.

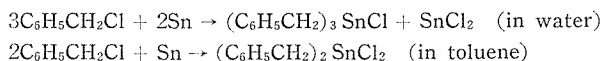
The preparation of synthetic estrogens. IX. 3,3-disubstituted derivatives of hexestrol. Keiiti Sisido, Yoko Udo, Hitosi Nozaki and Elwood V. Jensen. *J. Org. Chem.* **26**, 1227 (1961).—3,3'-Dihalohexestryl dimethyl ethers were prepared from the corresponding *m*-halo-*p*-methoxypropiphenones through reduction to the carbinol, bromination and the subsequent condensation of the Wurtz type. 3,3'-Difluoro- and 3,3'-dichlorohexestryl dimethyl ethers were demethylated smoothly by hydriodic acid, but similar treatment of 3,3'-dibromohexestryl dimethyl ether resulted in dehalogenation to give hexestrol. 3,3'-Dihalogenated butestrols were synthesized similarly. The Friedel-Crafts reaction of hexestryl dimethyl ether with various

acids chlorides furnished the corresponding 3,3'-diacylhexestryl dimethyl ethers which were reduced to the respective 3,3'-dialkylhexestrols. Certain other derivatives of nuclear substituted hexestrols are described.

Structure of thujopsene and hinokiic acid. Keiiti Sisido, Hitosi Nozaki and Takesi Imagawa. *J. Org. Chem.* **26**, 1964 (1961).—Ozonolysis of thujopsene afforded a new C_{15} -keto aldehyde (Va), which was cyclized to an α,β -unsaturated aldehyde (VIa'). Reactions and NMR spectra of these compounds supported the thujopsene structure Ia of Erdtman and others. Suggestions have been made that the plausible configuration of the angular methyl group in thujopsene should be *trans* with respect to the cyclopropane methylene group.

Partial asymmetric synthesis in the Darzens reaction. Keiiti Sisido, Osamu Nakanishi and Hitosi Nozaki. *J. Org. Chem.*, **26**, 4878 (1961).—The Darzens reaction of either (–)-menthyl or (+)-bornyl chloroacetate with acetophenone is accompanied by a partial asymmetric synthesis, as this is shown by reduction of the resulting ester with lithium aluminum hydride to (–)-3-phenylbutane-1,3-diol of varying optical activities. Interestingly the predominant configuration of the asymmetric center newly formed has been found to be the same in both cases. Ethanolysis of methyl or bornyl glycidate thus prepared affords the corresponding ethyl ester, which is dextrorotatory and can be transformed into (–)-3-phenylbutane-1,3-diol in optical yields comparable to those in direct hydride reduction. Possible mechanism leading to this asymmetric synthesis is discussed.

Direct synthesis of organotin compounds. I. Di- and tribenzyltin chlorides. Keiiti Sisido, Yosiyuki Takeda and Ziro Kinugawa. *J. Am. Chem. Soc.*, **83**, 538 (1961).—Benzyl chloride and tin powder suspended in water at 100° gave tribenzyltin chloride, while the same suspension in toluene at 111° afforded dibenzyltin chloride, both in good yields. Over-all equations of the reactions are



Direct synthesis of organotin compounds. II. Diallyltin dibromide and its derivatives. Keiiti Sisido and Yosiyuki Takeda. *J. Org. Chem.*, **26**, 2301 (1961).—Diallyltin dibromide was prepared by the reaction of allylbromide with tin powder in boiling toluene. The catalytic effect of mercuric chloride and some organic bases on this reaction was examined and optimum conditions for preparation were determined. Allylic rearrangements in this reaction were investigated. The same reaction in boiling water or butanol yielded propylene.

The Friedel-Crafts reaction of *o*-xylylene bromide. Keiiti Sisido, Yoko Udo, Tatuo Nakamura and Hitosi Nozaki. *J. Org. Chem.*, **26**, 1368 (1961).—The Friedel-Crafts reaction of *o*-xylylene bromide with benzene in the presence of aluminum chloride was found to afford a mixture of anthracene and diphenylmethane. Similar reaction with toluene gave a eutectic mixture of 2,6- and 2,7-dimethylantracenes besides 3,4'-dimethyldiphenylmethane, while *o*-xylene afforded 3,4-dimethyl- and 3,3', 4,4'-tetramethyldiphenyl-methanes. No anthracene derivative was isolated in

the last mentioned reaction. The condensation of *o*-xylene bromide with benzene by means of titanium tetrachloride resulted in the formation of *o*-dibenzylbenzene, neither anthracene nor diphenylmethane being isolated. The use of ferric chloride catalyst gave a mixture of *o*-dibenzylbenzene and diphenylmethane, while the latter hydrocarbon was a sole product in the reaction with stannic chloride. Boron trifluoride was found to be inactive in this reaction.

9,10 endo-o/Xylylene-9,10-dihydroanthracene. Keiiti Sisido, Yoko Udo and Hitosi Nozaki. *J. Org. Chem.*, **26**, 584 (1961).

Cyclopropanes. XI. Solvent effect in partial asymmetric synthesis. Yuzo Inouye, Shuji Inamasu, Minoru Ohno, Toshio Sugita and H. M. Walborsky. *J. Am. Chem. Soc.*, **83**, 2962 (1961).—Potassium *t*-butoxide-catalyzed Michael-type condensation of (–)-menthyl chloracetate with ethyl acrylate afforded, after saponification of the condensation product, (–)-trans-cyclopropane-1,2-dicarboxylic acid in non-polar solvents such as toluene, benzene, ether, *n*-octane, decalin and cyclohexane, whereas in polar solvents such as dimethylformamide, dimethylsulfoxide, hexamethylphosphortriamide, monoglyme and nitrobenzene, the same reaction gave the enantiomeric (+)-trans-cyclopropane-1,2-dicarboxylic acid. (See also, this Bulletin, **39**, 415 (1961).)

Blätteralkohol. IX. Eine einfache Synthese und Konfiguration des Blätteraldehyds. Akikazu Hatanaka und Minoru Ohno. *Agr. Biol. Chem.*, **25**, 7 (1961).—Blätteraldehyd wurde durch die einfachste, ergiebigste Synthese dargestellt. Demnach wurde es aufgeklärt, daß die Konfiguration des natürlichen Blätteraldehyds trans-Form ist.

Biochemistry

Studies on the cellulose decomposing organisms. I. Isolation of bacteria from soil and onion. Masayuki Ikemiya, Juichiro Yagi and Takaharu Osumi. *Hakko Kogaku Zasshi*, **39**, 148 (1961), in Japanese.—Two strains of cellulose decomposing bacteria were isolated. T-2 strain isolated from soil appears to be closely related to *Cellulomonas fimi* (McBeth et Scale), although difference is observed in gelatine liquefaction. T-4 strain isolated from onion has close resemblance to *Cellulomonas uda* (Kellerman), but the former produces gas very scantily from carbohydrates if any. The strains attack filter paper readily, while do cotton and saw dust very slowly.

Studies on the cellulose decomposing organisms. II. Isolation of bacteria from soil. Masayuki Ikemiya, Juichiro Yagi and Takaharu Osumi. *Hakko Kogaku Zasshi*, **39**, 281 (1961), in Japanese.—Two strains, I-1 and I-3 were isolated from soil in Osaka, and the former was presumed to belong to *Cellvibrio*, while the latter was found to resemble *Cellvibrio vulgaris* Stapp and Bortels. They attacked cellophane and filter paper readily, while did cotton and wood saw dust very slowly.